

Possible centers of broadband near-IR luminescence in bismuth-doped solids: Bi^+ , Bi_5^{3+} , and Bi_4

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Subvalent bismuth centers (interstitial Bi^+ ion, Bi_5^{3+} cluster ion, and Bi_4^0 cluster) are examined as possible centers of broadband near-IR luminescence in bismuth-doped solids on the grounds of quantum-chemical modeling and experimental data.

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I. INTRODUCTION

Near-IR broadband (1100 – 1400 nm) luminescence in bismuth-doped glasses discovered in Ref. [1] is being studied intensively. By now the luminescence has been observed in many bismuth-doped glasses, such as aluminosilicate (e.g. [1–6]), aluminogermanate (e.g. [3, 7–9]), alumoborate (e.g. [8, 10]), alumophosphosilicate, alumophosphate, alumophosphoborate (e.g. [3, 11, 12]), chalcogenide [13, 14], in several bismuth-doped crystals (RbPb_2Cl_5 [15], $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ cordierite [16], BaB_2O_4 [17], BaF_2 [18], $\text{Ba}_2\text{P}_2\text{O}_7$ [19], $\text{Bi}_5(\text{AlCl}_4)_3$ [20]), and in FAU-type (e.g. [21]) and Y-type [22] zeolites. The bismuth-related IR luminescence is used successfully in laser amplification and generation (e.g. [23, 24]).

However there is no commonly accepted model of the IR luminescence center. Several models are suggested, such as electronic transitions in Bi^0 interstitial atoms [25], in Bi^+ [10–13, 21, 22, 26], Bi^{2+} [13] and Bi^{5+} [2, 3, 9] interstitial ions, in BiO interstitial molecules [4], Bi_2 , Bi_2^- and Bi_2^{2-} interstitial dimers [5, 7, 14, 16, 27], in other neutral bismuth clusters [7], in Bi_5^{3+} cluster ions [20, 22, 26, 28], BiO_4 complexes with tetrahedral coordination of the central bismuth ion [29], in oxygen-coordinated complexes formed by pairs of threefold coordinated bismuth atoms [30], in complexes formed by Bi^+ or Bi^{2+} substitutional or interstitial ions with certain defect centers, such as anion vacancies [31].

Recently subvalent bismuth centers such as Bi^+ single-charged bismuth ion and Bi_5^{3+} cluster ion have attracted considerable attention as possible sources of the near-IR luminescence [20, 26, 28]. In this paper we examine three subvalent bismuth centers basing on experimental data available and our quantum-chemical modeling. Namely, the above-mentioned (interstitial) Bi^+ ion and Bi_5^{3+} cluster ion, and (as a novel suggestion) Bi_4^0 cluster are studied.

II. CALCULATIONS

Configuration and electronic states of Bi_5^{3+} and Bi_4^0 clusters were calculated using GAMESS (US) quantum-chemical code [32]. Firstly, ground state DFT calculations of the clusters were performed using B3LYP1 functional (Becke+Slater+Hartree-Fock exchange and Lee-Yang-Parr+Vosko-Wilk-Nusair (5) correlation — see GAMESS (US) manuals [32] for details) and effective core potentials (ECP) and bases of three types developed in Refs. [33–35] with one Huzinaga’s polarization d-type function [36] added in each basis.

The calculated molecular orbitals were then used to obtain the final molecular wave functions by means of perturbation theory with multiconfigurational self-consistent-field reference functions. These final wave functions and corresponding eigenvalues were used to calculate eigenfunctions and energies of the ground and excited states of the clusters by method of configuration interaction in active orbitals space with spin-orbit interaction taken into account.

Multiconfiguration complete active space self-consistent field (MC-CASSCF) and multireference configuration interaction (MRCI) were used to calculate electronic states of Bi_5^{3+} and Bi_4^0 clusters. Separate CASSCF calculations were performed for the ground state and the lowest excited state of each cluster. Then MRCI calculations were made with all CASSCF configurations with coefficients large enough taken into account (see GAMESS (US) manuals for details). Additionally, single and double excitations from these configurations were allowed.

Evaluative calculation of optical spectra in external electric field and of ground-state optical absorption spectra (to verify independently the results of configuration interaction calculations) were performed by time-dependent density functional theory (TDDFT) method using Octopus program [37] and Hartwigsen-Goedecker-Hutter pseudopotentials [38] with spin polarization and spin-orbit interaction taken into account. PBE density functional [39] was used in the ground-state calculation. In the Octopus code, to obtain the linear optical absorption spectrum of the system, all frequencies of the system are excited by giving certain (small enough) momen-

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tum to the electrons. Then the time-dependent Kohn-Sham equations evolves in real space for a certain real time [40] and the dipole-strength function (or the photo-absorption cross section) is obtained by a Fourier transform of the time-dependent dipole moment. Adiabatic LDA approximation is used in these calculations to describe exchange-correlation effects. The Octopus code uses real-space uniform grid inside the sum of spheres around each atom of the system (a single one in our case). The sphere radius and the grid spacing were taken to be was 8.0 and 0.25 Å, respectively, in our calculations. The real-time propagation was performed with $2 \cdot 10^4$ time steps with the total simulation time of about 20 fs. The Fourier transform was performed using third-order polynomial damping (see [37] for details of the code).

III. ELECTRONIC STATES AND OPTICAL SPECTRA OF FREE BISMUTH SPECIES

A. Bi^+ bismuth ion

The optical absorption and emission of free singly charged positive bismuth ion, Bi^+ , are well known (see, for example, [41]). The ground state and two low-lying excited states with energies about 13325 and 17032 cm^{-1} are known to be formed owing to spin-orbit splitting from the ^3P term. The electronic configurations of these three states are $6p_{1/2}^2$ ($J = 0$), $6p_{1/2}^1 + 6p_{3/2}^2$ ($J = 1$), and $6p_{1/2}^1 + 6p_{3/2}^2$ ($J = 2$), respectively. The subsequent excited states with much greater energy (about 33940 and 44175 cm^{-1}) correspond to ^1D and ^1S terms with electronic configurations $6p_{3/2}^2$ ($J = 2$) and $6p_{3/2}^2$ ($J = 0$), respectively. Obviously, all the electric dipole (E1) transitions between the states just listed are forbidden, only magnetic dipole (M1) and electric quadrupole (E2) transitions being allowed. In particular, the ground state of Bi^+ ion is characterized by weak absorption at wavelengths about 750, 585 and 295 nm corresponding to M1 and E2 transitions from the ground state to three lowest excited states. The most long-wavelength luminescence in Bi^+ ion corresponds to the M1 transition from the first excited state to the ground one (Fig. 1 (a)). Obviously, there is no Stokes shift in free ion.

In Ref. [42] absorption spectra of Bi^+ ion in chlorides melts have been studied and interpreted basing on crystal field theory. According to this study, two lowest excited states of the ion are split by the crystal field in two and three levels, respectively. As a result, the transition energy decreases significantly, and bands around 900, 785, 660–690, and 585 nm are observed in the absorption spectrum (Fig. 1 (b)).

Unfortunately, calculation of Bi^+ ion spectra (both free ion and one in electrostatic field) with the spin-orbit interaction taken into account presents severe computational problems using GAMESS (US) program. Our conservative estimates and evaluative calculations performed

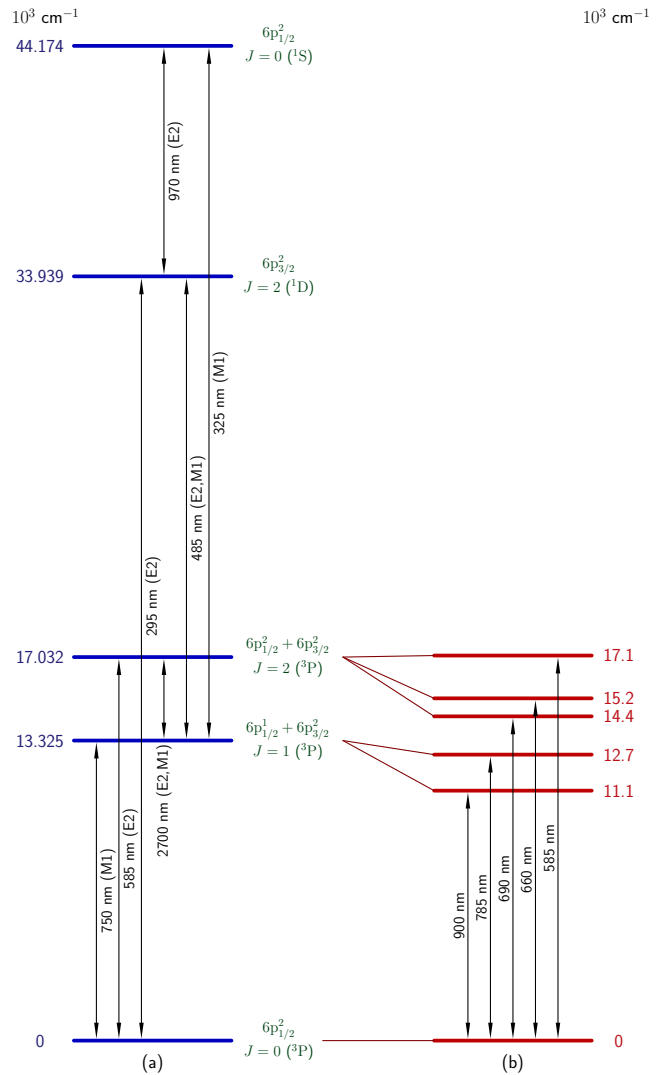


Figure 1. Experimental states and transitions in (a) free Bi^+ ion [41] and (b) Bi^+ ion in AlCl_3 – NaCl eutectic [42].

by the TDDFT method using Octopus code causes us to anticipate that the wavelength of the lowest-energy transition does not exceed 1000 nm essentially. Such a conclusion is consistent with the results of Ref. [42].

B. Bi_5^{3+} cluster ion

Our calculations prove the electronic ground state of Bi_5^{3+} cluster ion to be a singlet. In this state, the ion symmetry is found to be D_{3h} (Fig. 2 ((a))). Interatomic distances $\text{Bi}_{ax} - \text{Bi}_{eq}$ and $\text{Bi}_{eq} - \text{Bi}_{eq}$ between axial, Bi_{ax} , and equatorial, Bi_{eq} , bismuth atoms are 3.089 Å and 3.325 Å, respectively. This agrees well with both experimental and calculated data for free Bi_5^{3+} cluster ion [48]. In Fig. 3 (a) are shown the calculated scheme of the Bi_5^{3+} cluster ion levels and transitions between them. In

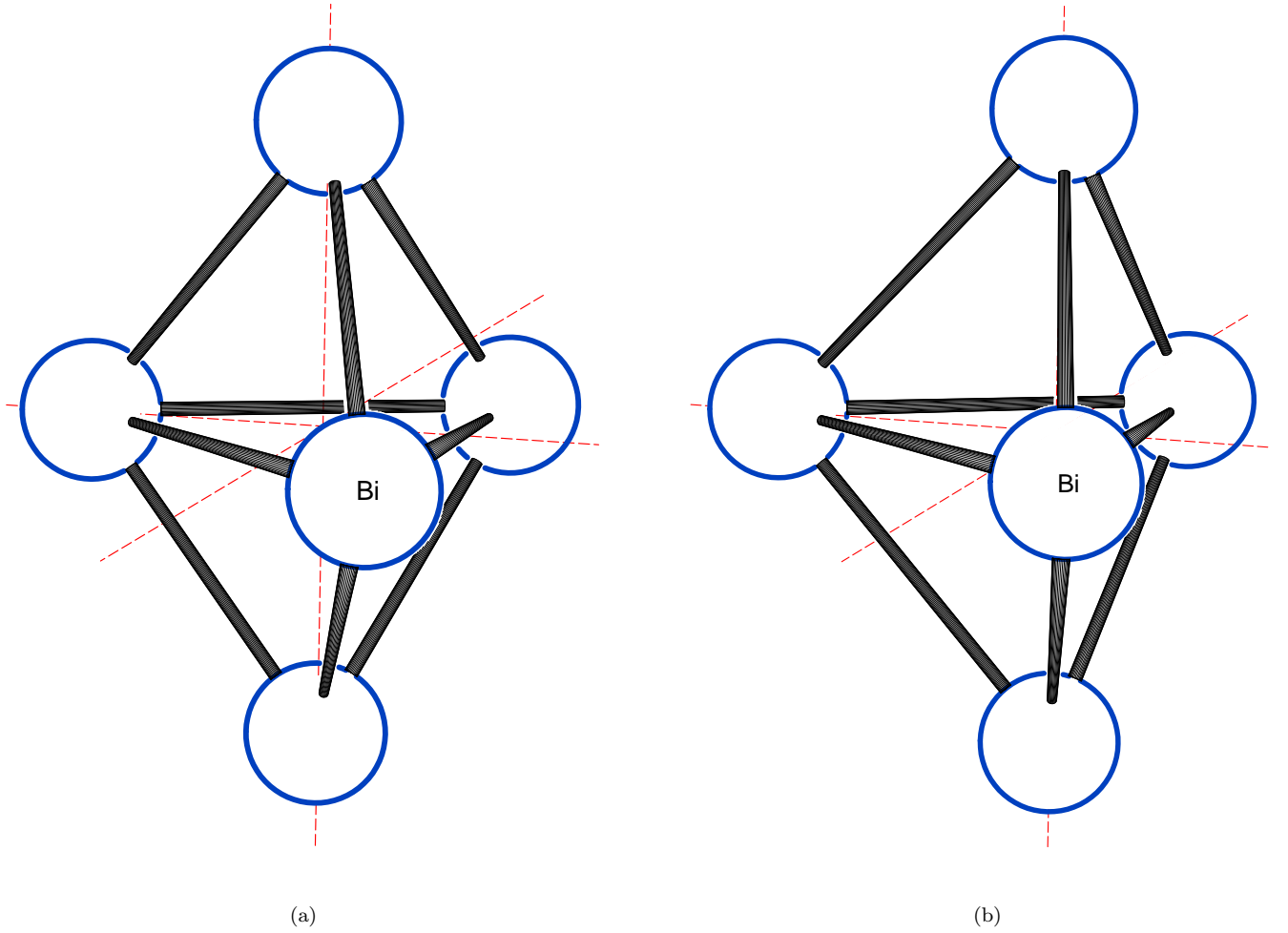


Figure 2. Calculated configurations of free Bi_5^{3+} cluster ion: (a) ground-state singlet (D_{3h} symmetry), (b) first excited-state triplet (C_{2v} symmetry).

the ground state configuration, the electronic states are classified according to irreducible representations of the D_{3h} group. From the ground state with the A'_1 symmetry E1 transitions are allowed to excited states with E' and A'_2 symmetry, giving rise to absorption at 750, 585 and 450 nm wavelengths (shown by solid arrows in the Fig. 3). When perturbed by an external electrostatic (crystalline) field, E1 transitions from the ground state to the excited states with E'' symmetry become slightly allowed corresponding to absorption at wavelengths of about 835 and 730 nm (displayed as dashed arrows in Fig. 3). It should be noted that in the absence of spin-orbit interaction all the excited states in Fig. 3 correspond to the first excited triplet. These results are in good agreement both with the experimental data available on Bi_5^{3+} cluster ions optical absorption [48, 50], and with the results of our TDDFT calculations using the Octopus code shown in Fig. 4. As well those agree reasonably with experimental data for $\text{Bi}_5(\text{AlCl}_4)_3$ crystal [20].

Fig. 2 ((b)) shows the calculated configuration of Bi_5^{3+} cluster ion in the lowest excited state. To our knowledge,

the calculation of configuration of this ion in an excited state is performed for the first time. Being excited to this state, Bi_5^{3+} cluster ion undergoes deformation corresponding to E'' irreducible representation of the D_{3h} group. As a result, the cluster ion symmetry is reduced to C_{2v} . One of the $\text{Bi}_{ax} - \text{Bi}_{eq}$ interatomic distances is increased to 3.363 Å, the other two distances are decreased to 3.043 Å, and corresponding $\text{Bi}_{eq} - \text{Bi}_{eq}$ distances become 3.332 Å and 3.362 Å, respectively. Calculated levels of Bi_5^{3+} cluster ion in the configuration of its lowest excited state, transitions to the ground state and relative lifetimes are shown in Fig. 3 (b). In our calculations two E1 transitions to the ground state are found in this configuration. Those lead to two bands of IR luminescence in 1200 – 1290 nm range with lifetimes differing by an order of magnitude, which may be called "slow" and "fast" components (unfortunately, only relative lifetimes may be estimated in our calculations). It should be remarked that such two components of bismuth-related IR luminescence have been observed repeatedly (see e.g. Refs. [3, 6, 28]).

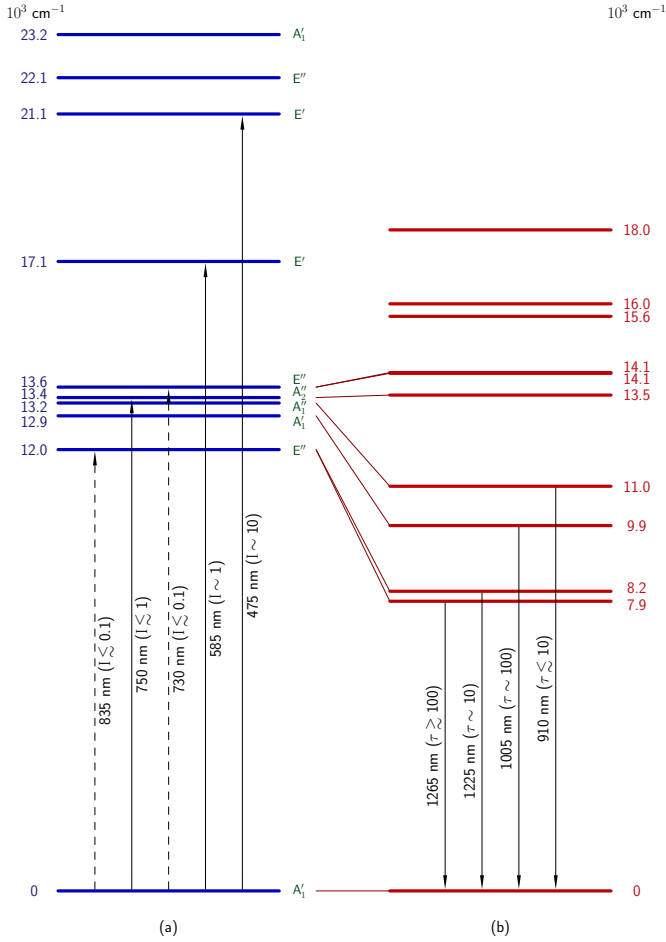


Figure 3. Calculated states, excitation transition rates and luminescence lifetimes in free Bi_5^{3+} cluster ion: (a) ground state, (b) 1-st excited state (transition rates and lifetimes in relative units).

Furthermore, there are luminescence bands near 1000 and 900 nm (as well "slow" and "fast", respectively). These results are also confirmed in our TDDFT calculations.

C. Bi_4^0 cluster

According to our calculation the electronic ground state of Bi_4^0 cluster turns out to be a singlet. As seen from Fig. 5 ((a)), in this state the Bi_4 cluster is a regular tetrahedron (T_d symmetry). Bi–Bi interatomic distances are found to be 3.104 Å in agreement with the results of Ref. [46]. Fig. 6 (a) presents the calculated scheme of levels, transitions between those and the relative intensity of the transitions in the Bi_4^0 cluster. The electronic states of the cluster in the ground state configuration correspond to T_d group irreducible representations. Thus, the ground state has A_1 symmetry. From the ground state E1 transitions only to the excited state with F_2

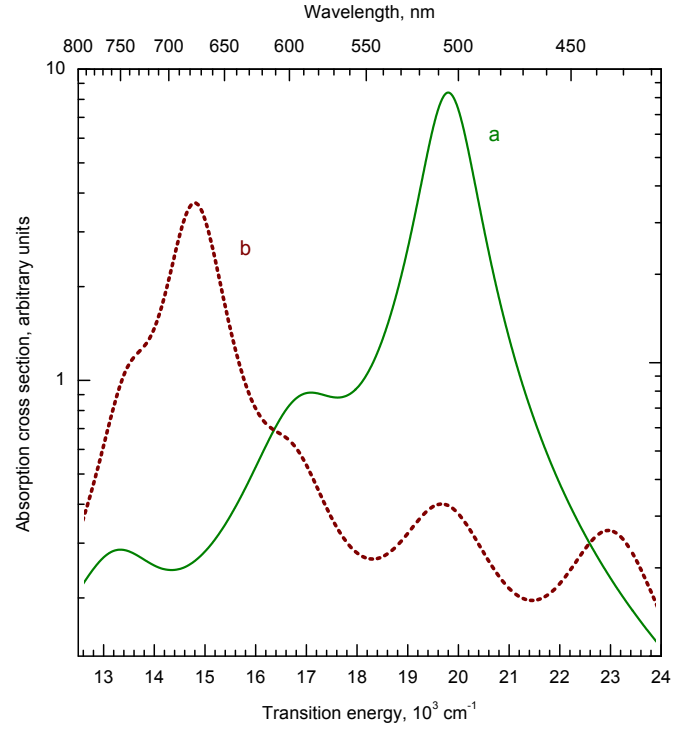


Figure 4. Absorption cross section of (a) Bi_5^{3+} and (b) Bi_4^0 clusters calculated by TDDFT method.

symmetry are allowed. Those correspond to absorption bands near 670 and 420 nm (solid arrows in Fig. 6). In an external electrostatic field E1 transitions from ground state to the states with A_2 , F_1 , and E symmetry become slightly allowed as well, and absorption at wavelengths of about 735, 590 and 525 nm arises (dashed arrows in Fig. 6). The first four excited states are formed due to spin-orbit splitting of the 3F_2 triplet state, and the next ones arise from 1F_2 and 1F_1 singlet states.

The energies of states and transitions in Bi_4^0 cluster obtained in our calculation agree well with the results of the calculations in Ref. [46]. However the results differ in the order of levels: the states with E and A_2 symmetries turn out to be interchanged. On the other hand, the transition energies obtained in quantum-chemical calculations, both our and that of Ref. [46], agree closely with our TDDFT calculation (Fig. 4).

Excitation to the lowest excited state with E symmetry is accompanied by rearrangement of the cluster configuration resulting in the cluster symmetry reduced to C_{2v} . The length of one of the tetrahedron edges (Bi–Bi distance) is increased to 3.378 Å and the length of the opposite edge is reduced to 3.005 Å, while the other Bi–Bi distances are reduced to 3.082 Å (Fig. 5 ((b))).

In Fig. 6 (b) are shown the calculated levels together with transitions to the ground state and their relative lifetimes for the lowest excited state configuration of Bi_4^0 cluster. According to the calculations, in this configuration the most long-wavelength luminescence in the 950

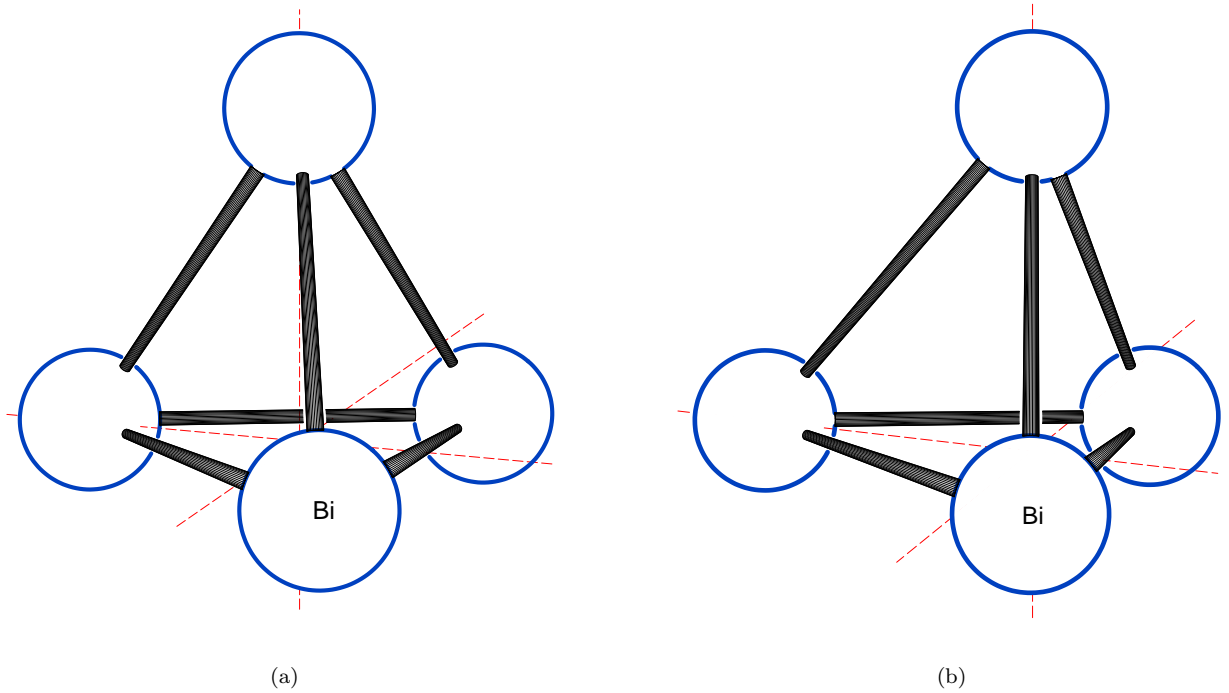


Figure 5. Calculated configuration of free Bi_4^0 cluster: (a) ground-state singlet (T_d symmetry), (b) first excited-state triplet (C_{2v} symmetry).

– 1040 nm range contains two components (“slow” and “fast” in the same degree as above) corresponding to E1 transitions from the first and second excited states to the ground one. Furthermore, E1 transitions from two higher excited states to the ground state can lead to the “fast” luminescence near 830 and 660 nm. Our TDDFT calculations with the Octopus code yield similar results.

IV. BISMUTH SPECIES IN SILICATE GLASS NETWORK

To study the possibilities of occurrence of Bi^+ ion, Bi_5^{3+} cluster ion, and Bi_4^0 cluster in silicate glass network, we performed quantum-chemical modeling of these centers in ring interstitial sites of silica glass network using cluster approach. In the clusters there are either one or two six-member rings formed by four SiO_4 tetrahedra. Dangling bonds of the outer oxygen atoms in the clusters were saturated with hydrogen atoms. The bismuth species was placed initially at the center of the ring(s) and then the complete geometry optimization was performed. Details of computational techniques were described above. Standard 3-21G basis was used for saturating hydrogen atoms.

A. Bi^+ bismuth ion

In our calculations equilibrium position of Bi^+ ion in silicate glass network is found in interstitial sites formed by six-member rings, Bi^+ ion being located near the rings axis between the rings planes. However, the calculations prove this position of Bi^+ ion to be not stable enough: even relatively small displacement of the ion (not more than 10 % of the minimal distance to neighboring atoms) leads to further drift apart from the equilibrium position. Subsequent process is determined by the environment. Thus, in the regular ring interstitial Bi^+ ion moves towards one of the nearest oxygen atoms in the surrounding rings and threefold coordinated bismuth atom and threefold coordinated silicon atom are formed. If there are another Bi^+ ion(s) or Bi^0 atom(s) nearby, interstitial dimers or larger bismuth clusters are likely to arise instead. As an example, calculated position of Bi_2^+ dimer in six-member rings interstitial of aluminosilicate network is shown in Fig. 7. Some evidence is found in our calculations that Bi^+ ion may be stabilized in interstitial site of the silicate glass network by neighboring defects, such as oxygen vacancies.

Thus, although single interstitial Bi^+ ions may occur in the silicate glass network, their stability is poor and significant concentration of such ions seems hardly probable. On the other hand, small bismuth clusters or Bi^+ — defect complexes may be formed in the network interstitials, such clusters and complexes being quite stable.

It is notable that the luminescence Stokes shift which

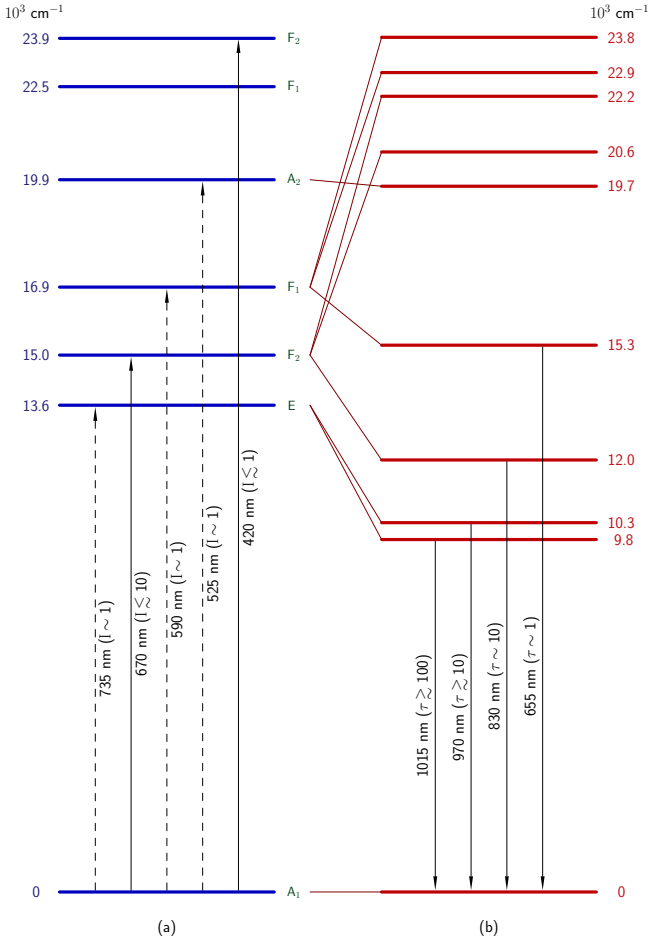


Figure 6. Calculated states, excitation transition rates and luminescence lifetimes in free Bi_4^0 cluster: (a) ground state, (b) 1-st excited state (transition rates and lifetimes in relative units).

vanishes in free Bi^+ ion should be expected to be low in the interstitial ion as well, but this is not the case for the above-mentioned clusters or complexes.

B. Bi_5^{3+} cluster ion

Geometric sizes of Bi_5^{3+} cluster ion are obviously too large to allow the ion to be incorporated in ring interstitial sites of silicate glasses. On the other hand, owing to significant electric charge the ion is very likely to react with the neighboring electronegative atoms.

Our calculations performed using the above-described cluster models confirm these considerations. It is found that Bi_5^{3+} cluster ion reacts with the bridging oxygen atoms of the network to form interstitial Bi_4^0 cluster and single Bi^{3+} ion nearby. The latter is then built into the glass network forming threefold coordinated bismuth atom. The resulting structure is shown in Fig. 8.

It should be realized that even Bi_5^{3+} ion is not able to

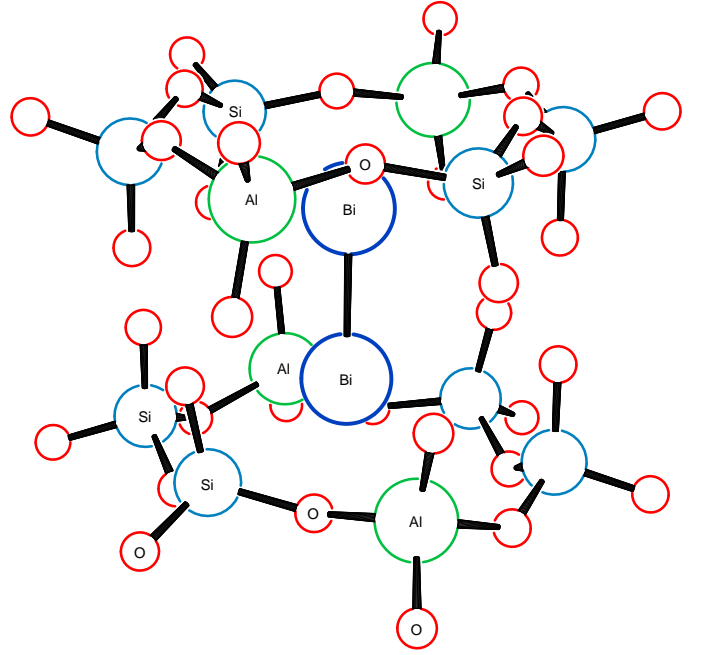


Figure 7. Calculated configuration of Bi_4^+ dimer in six-member ring interstitial of aluminosilicate glass network.

react with neighboring network atoms for whatever reason, the 3+ charge state of the Bi_5 cluster turns out to be unstable with respect to electron capture. We have calculated electron affinity of Bi_5^{3+} cluster ion by the above-described quantum-chemical methods in DFT level of theory and obtained closely agreed values for vertical and adiabatic electron affinities: $14.2 \text{ eV} \lesssim EA_v \lesssim EA_a \lesssim 14.6 \text{ eV}$.

These values significantly exceed not only the electron affinity of the silicate network ($\lesssim 1.2 \text{ eV}$), but its band gap width ($\lesssim 9 \text{ eV}$) as well. Hence Bi_5^{3+} cluster ion should capture electron in silicate host, the capture being possible not only from the conduction band, but from the valence band as well.

Thus, interstitial Bi_5^{3+} cluster ions occurrence should be recognized to be impossible in silicate hosts.

However, it seems reasonable to guess that Bi_5^{3+} cluster ion can occur in zeolite hosts due to extremely large size of their cage-like interstitials and stabilizing action of $(\text{AlO}_4)^{1-}$ tetrahedra similar to such action of $(\text{AlCl}_4)^{1-}$ ions in $\text{Bi}_5(\text{AlCl}_4)_3$ crystal [20].

C. Bi_4^0 cluster

The calculations have proved Bi_4^0 clusters to be able to occur in ring interstitials of silicate networks, despite the large size of the cluster. One such example is above-described formation of Bi_4^0 cluster from Bi_5^{3+} cluster ion. However threefold coordinated bismuth atom does not need to be present in the surrounding rings: according

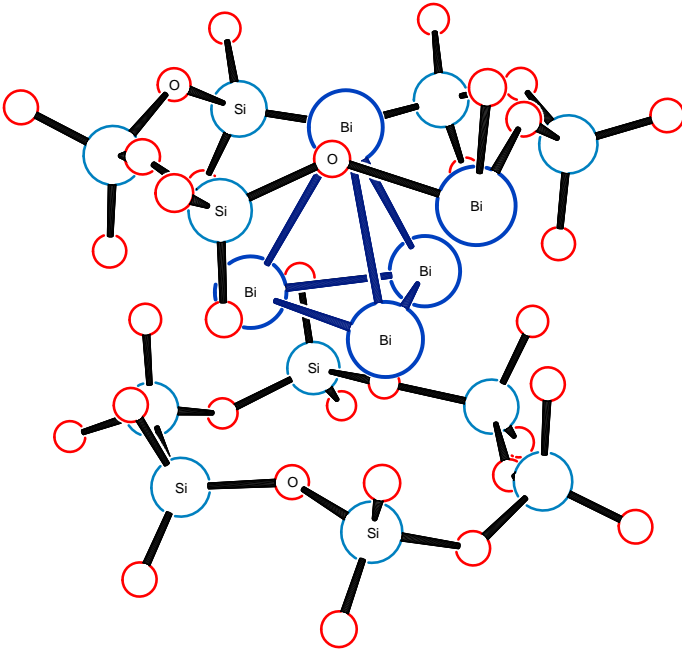


Figure 8. Calculated configuration of Bi_4^0 cluster in six-member ring interstitial of silica glass network.

to our modeling, a configuration quite similar to that shown in Fig. 8 arises as well in purely-silicate and aluminosilicate rings. Such positions of Bi_4^0 clusters in ring interstitials are found to be extremely stable. Even relatively large displacement and (or) rotation of the Bi_4^0 cluster, accompanied by its atoms shifted up to 50 % of interatomic distance do not make the above-mentioned configuration be destroyed.

Thus, Bi_4^0 clusters can occur in the ring interstitial of the pure-silicate network, and probably in certain binary silicate networks as well, such an interstitial position being extremely stable. Together with the fact the Bi_4^0 cluster binding energy is known to be abnormally high [47], this suggests the possibility of high concentration of such clusters in silicate hosts.

V. CONCLUSIONS

Both the experimental data available and the results of our calculations allow draw some conclusions concerning the origin of the above-mentioned IR luminescence centers in the bismuth-containing systems.

1. For Bi^+ singly-charged positive ion:

- (a) the lowest-energy transition wavelength does not exceed 1000 nm;
- (b) all the relatively long-wavelength transitions occur between electronic states originating (due to spin-orbit interaction) from the same

^3P term and hence intensities of both absorption and luminescence transitions are of the same order;

- (c) Stokes shift is low or even vanishes;
- (d) although there are equilibrium interstitial positions of Bi^+ ion in certain solids, single Bi^+ seems to be not stable enough, at least in oxide glasses networks.

Thus, single Bi^+ ion can be responsible for certain optical absorption bands in bismuth-containing systems, but can not be considered as a center of the IR luminescence.

2. For Bi_5^{3+} cluster ion:

- (a) IR luminescence spectrum accords well enough with the experimentally observed luminescence in bismuth-containing systems;
- (b) there are a number of bands in the absorption spectrum corresponding to the absorption observed in experiment;
- (c) in the absorption spectrum of free Bi_5^{3+} cluster ion there is no band at 500 nm, the most intense in experimental spectra of bismuth-containing systems;
- (d) large size, high electrical charge and high electron affinity of the Bi_5^{3+} cluster ion make it practically impossible for the ion to occur in a solid host other than, supposedly, zeolite.
- (e) in silicate glass the cluster ion can react with bridging oxygen atoms of the glass network forming threefold coordinated bismuth atom bound in the network and interstitial Bi_4^0 cluster.

Thus, Bi_5^{3+} cluster ion can be responsible for a number of absorption and IR luminescence bands in certain bismuth-containing systems, namely, ionic solutions and, possibly, zeolites, but not for those in silicate glasses.

3. For Bi_4^0 cluster:

- (a) in free Bi_4^0 cluster, IR luminescence occur only near 1000 nm wavelength, but under the influence of crystal field the wavelength can increase (up to 1100 – 1150 nm according to our estimations);
- (b) in the absorption spectrum of the cluster there are a number of bands corresponding to the absorption observed in experiment including the band at 500 nm. However, the band near 670 nm is the most intense, which is hardly consistent with experimental data;
- (c) there are equilibrium positions of Bi_4^0 cluster in sufficiently large interstitial sites in solid hosts (e.g. in the ring interstitials of oxide

glasses networks), these positions being quite stable.

Thus, Bi_4^0 cluster can be responsible for a number of absorption and IR luminescence bands in the bismuth-containing systems.

4. If in a bismuth-containing system both Bi^+ ions and Bi_5^{3+} cluster ions or (and) Bi_4^0 clusters occur simultaneously, one would expect mutual excitation transfer between the centers of different types.

Thus, none of the Bi^+ , Bi_5^{3+} , and Bi_4^0 centers alone can not give rise to the experimental IR luminescence and absorption spectra typical for the bismuth-doped solids. On the other hand, these spectra of ionic solutions are likely to be caused by Bi^+ and Bi_5^{3+} ions together.

It is our opinion that the experimental data available are consistent with the following speculations involving the centers under consideration. In solid hosts, most likely both Bi^+ ions and Bi_4^0 clusters occur in interstitial sites (the latter in sufficiently large interstitials, in the ring ones particularly). Moreover, it is conceivable that

interstitial Bi^+ ions could form pairs with each other or with interstitial Bi^0 atoms. In ionic solutions, Bi^+ ions and Bi_5^{3+} cluster ions most likely occur. Excitation transfer from Bi^+ ions to other bismuth centers is expected to proceed in all the cases.

On the other hand, it should be emphasized that no experimental data nor calculation results suggest that in the bismuth-doped systems there are no IR luminescence centers other than those considered in this paper. In particular, we persist in the belief that negatively charged bismuth dimers, Bi_2^- and Bi_2^{2-} [16, 27], and dimers (or even more complex clusters) of Bi^+ or Bi^{2+} ions and some intrinsic defect centers [31] are quite possible to occur in bismuth-doped solids. Moreover, it seems reasonable to expect that bismuth centers of several types may be formed concurrently in these solids. The assumptions concerning existence of several types of IR luminescence centers in bismuth-doped solids is supported by significant variation of both absorption spectra and IR luminescence spectral and temporal dependencies, with preparation conditions etc. observed in various systems.

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